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Copolymers of 2-hydroxy-3-(*N*-methyl-*N*-phenylamino)propyl methacrylate with methyl methacrylate and their microstructure

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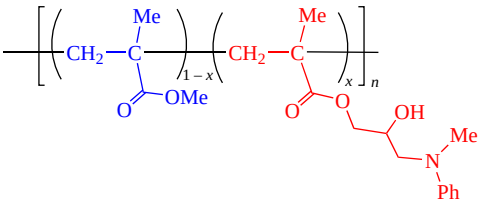
A precursor for the production of azo chromophores, *viz*. 2-hydroxy-3-(*N*-methyl-*N*-phenylamino)propyl methacrylate, was prepared and characterized. Its copolymerization with methyl methacrylate was carried out and the copolymerization constants were determined: for 2-hydroxy-3-(*N*-methyl-*N*-phenylamino)propyl methacrylate, $r_1 = 0.50$; for methyl methacrylate, $r_2 = 0.93$. The average block lengths of monomers of the same type depending on the composition of the copolymer were estimated.



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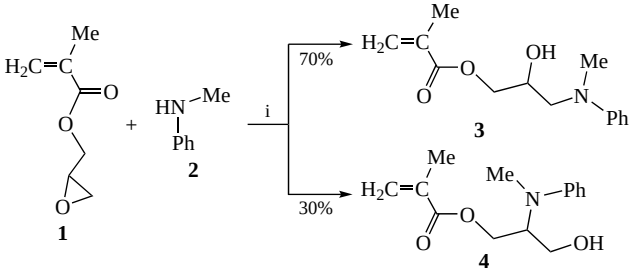
The development of new nonlinear optical (NLO) polymers for applications in photonics and optoelectronics is of great importance for modern materials science.[1–3] Methacrylic copolymers with chromophores in the side chain attract attention due to the simplicity of their synthesis and the wide possibility of functionalization with chromophores of various structures. In addition, methacrylic polymers provide good properties of the polymer matrix, for example, high optical transparency, low loss during light propagation, as well as processability in the development of optoelectronic devices. Azo chromophores often serve as molecular sources of the NLO response of polymer material.[2] The chromophores can be introduced into methacrylic polymers in various ways: either by radical polymerization of chromophore-containing methacrylates with vinyl comonomers,[4–9] or by functionalization of reactive methacrylic copolymers using polymer-analogous transformations,[10,11] or by azo coupling.[12,13] When obtaining polymers with chromophores in the side chain, the interest is usually associated with the synthesis of copolymers and the study of their quadratic NLO characteristics. There are not so many works on the study of the reactivity of chromophore-containing methacrylic monomers, and even more so of methacrylic precursors, in copolymerization reactions with vinyl comonomers, and on the study of the microstructure of the resulting copolymers.[4–7,14–16]

Earlier,[6] using the acid chloride-free technology we performed a reaction between glycidyl methacrylate **1** and *N*-methylaniline **2** and obtained the corresponding aniline-containing methacrylate (Scheme 1). After azo coupling reaction, we accessed a chromophore-containing methacrylic monomer, namely, 4′-[*N*-methyl-*N*-(3-methacryloyloxy-2-hydroxypropyl)amino]-4-nitroazobenzene (MAZ), and its radical copolymerization with methyl methacrylate was studied.[6] We have found that according to the ^{1}H NMR spectrum [Figure 1(*a*)], the addition of *N*-methylaniline **2** to glycidyl methacrylate **1** occurred in two directions: either at α or at β position of the epoxy ring (see Scheme 1). The resulting reaction mixture consisted of regioisomeric 2-hydroxy-3-(*N*-methyl-*N*-phenylamino)propyl methacrylate **3** (α-AMA) and 3-hydroxy-2-(*N*-methyl-*N*-phenylamino)propyl methacrylate **4** (β-AMA) in a ratio of 70 : 30, respectively. In the reported study,[6] this mixture was processed further followed by the isolation of the target azo compound using column chromatography. The mixture was also tested for preparing chromophore-containing methacrylic homopolymers[13] and copolymers with methyl methacrylate (MMA)[13,17] followed by azo functionalization. However, individual α-AMA **3** may serve as more promising precursor for the synthesis of various reactive azo chromophores, so its isolation from the reaction mixture and the study of its reactivity in the copolymerization reaction is of special interest.

Herein, some physicochemical characteristics of α-AMA **3** were determined, and its reactivity during copolymerization with MMA was studied. Individual isomer α-AMA **3** was isolated from the reaction mixture by column chromatography using chloroform/ethyl acetate eluent in a ratio of 4 : 1. The structure of α-AMA was confirmed by ^{1}H NMR [Figure 1(*b*)] and IR spectroscopy (see Online Supplementary Materials). The signals in the regions of 6.07 ppm, 5.59 ppm (=CH_2), 2.98 ppm (–NCH_3) and 1.88 ppm (C–CH_3) corresponding to the β-isomer **4** are absent in the ^{1}H NMR spectrum.



Scheme 1 *Reagents and conditions*: i, 95 °C, 14 h.

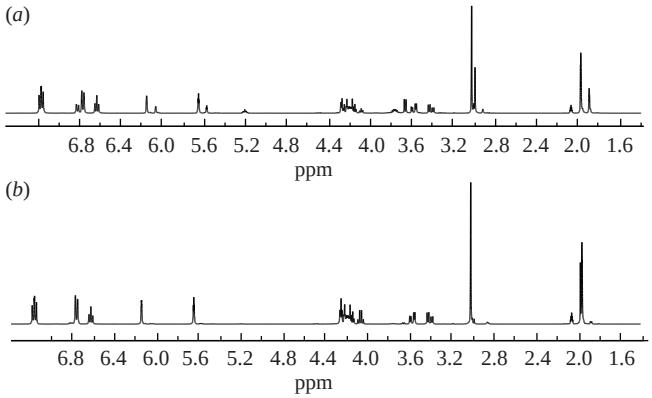
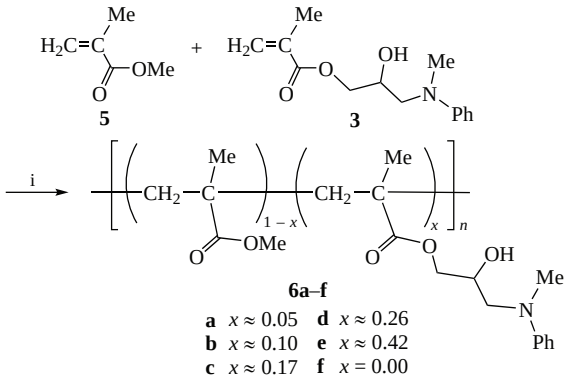


Figure 1 ^{1}H NMR spectra of (*a*) the reaction mixture and (*b*) α-AMA.

The radical copolymerization of MMA **5** with α-AMA **3** in a DMF solution at 70 °C afforded copolymers **6a**–**e** with different content of aniline methacrylate (5–50 mol%) depending on the ratio of monomers taken (Scheme 2). The choice of polymerization conditions, namely, solvent, amount of initiator, concentration of comonomers, was determined by the desire to compare the results obtained with the parameters for MMA-MAZ.[6] Comparison of the ^{1}H NMR spectra of copolymers **6a**–**e** (see Online Supplementary Materials) and **3** [Figure 1(*b*)] indicates the complete disappearance of the double bonds of the monomer, the signal for the CH_3 group undergoes an upfield shift (~0.7 ppm). New signals appear from the OCH_3 group of MMA (3.66 ppm); the main chain protons appear in the range of 0.8–2.0 ppm. The formation of copolymers was also confirmed by IR spectra (see Online Supplementary Materials). In the spectra of copolymers, the absorption band at 1647 cm^{-1} typical of C=C bond is absent, the carbonyl group (1719 cm^{-1} typical of the conjugated one) undergoes a slight shift to 1731 cm^{-1}; absorption bands for hydroxy groups (3519 cm^{-1}) and aromatic fragments (1601, 1508 cm^{-1}) appear. With increasing AMA content in the copolymer, the intensity of the absorption bands for OH and Ar groups increases, and this dependence is linear (see Online Supplementary Materials, Figure S13). Some physicochemical characteristics of the obtained copolymer were determined (Table 1). Satisfactory agreement is observed between the copolymer composition determined by ^{1}H NMR and elemental analysis for nitrogen. Molecular weight and polydispersity of copolymers **6a**–**e** increase with the α-AMA units content in contrast to the MMA-MAZ,[6] for which, with an increase in the number of MAZ units, the molecular weight of the copolymers decreased from 28000 Da (11 mol% MAZ) to 19900 Da (38 mol% MAZ), which was due to the known chain transfer reaction to the chromophore, most likely, with the participation of a nitro group.[6] Copolymer GPC data is characterized by unimodal molecular weight distribution (see Online Supplementary Materials, Figure S14).



Scheme 2 *Reagents and conditions*: i, DMF, AIBN, 70 °C, 2.5 h.

Table 1 Some physicochemical characteristics of the obtained MMA-α-AMA copolymers **6**.

Copolymer	Content of α-AMA units			$M_w \times 10^{-3}$/ Da	M_w/M_n	T_g/ °C	$T_{10\%}$/ °C
	in initial mixture	in copolymer					
		from ^{1}H NMR	from elemental analysis[a]				
6a	0.05	0.045	0.058	23.8	1.8	102	269
6b	0.10	0.096	0.11	27.4	2.1	102	279
6c	0.20	0.17	0.16	28.3	2.2	114	277
6d	0.30	0.24	0.28	33.5	2.3	114	287
6e	0.50	0.39	0.45	39.2	2.7	113	292
6f	0	–	–	17.6	1.8	104	300

[a] Derived from nitrogen percentage.

Glass transition temperature grows insignificantly with the increase of the content of α-AMA units in the copolymer, which may be due to a slight increase in the molecular weight of the copolymers (see Table 1). The thermal stability of copolymers **6** almost does not change with an increase in the content of α-AMA units.

Based on the dependence of the composition of copolymers on the composition of the initial monomer mixture, the reactivity ratios of monomers were determined using the Kelen–Tüdös equation,[18] (see also refs. 6, 14 and 19–21) to calculate constants at deep degrees of conversion. The obtained values of the reactivity ratios, $r_1 = 0.50$ (for α-AMA **3**) and $r_2 = 0.93$ (for MMA **5**) indicate a higher reactivity of MMA and the occurrence of 'azeotropic' copolymerization, as well as the formation of a copolymer with a statistical distribution of monomer units. Good agreement between the theoretical estimation of the dependence of the copolymer composition *vs.* the composition of the initial mixture, obtained using these reactivity ratios, and the corresponding experimental data was observed (see Online Supplementary Materials, Figure S15). Previously,[6] we indicated that the addition of an azobenzene bridge fragment and acceptor nitro-group to an aniline fragment with the production of azo chromophor methacrylate (MAZ) led to an increase in its reactivity in the copolymerization reaction with MMA ($r_{MAZ} = 0.87$ and $r_{MMA} = 0.85$).

The properties of copolymers largely depend not only on the composition, but also on the distribution of units in macromolecules. Since the distribution of units in the copolymer is statistical in nature, the resulting copolymer should be a complex set of different microstructures. During the copolymerization reaction, the distribution of monomeric units within the macromolecule changes continuously. Therefore, when studying the regularities of copolymerization and the properties of copolymers, of great interest are easily calculated parameters that clearly evaluate the nature of the distribution of units in a polymer chain.

For binary copolymers, the widely used parameters are the average lengths $\bar{L}_{M_1}$ and $\bar{L}_{M_2}$ of blocks of identical units, the block parameter called the Harwood parameter, *R*, which defines the number of blocks of identical units per 100 units of the copolymer, and the probabilities of formation of various types of bonds. We have calculated these values using the data on the composition of copolymers and the corresponding reactivity ratios r_1 and r_2 for different compositions of the monomer mixture using the special equation (see Online Supplementary Materials, page S12); the obtained results are presented in Table S1. Analysis of the average length estimations of the units shows that in the α-AMA-MMA system with an aniline

methacrylate content in the initial mixture varying from 5 to 30 mol%, single α-AMA units are separated by rather extended MMA blocks; and only when the α-AMA content is 50 mol%, the length of the α-AMA blocks becomes practically equal to the length of the MMA blocks.

In conclusion, it can be assumed that since the probability of the formation of blocks consisting of α-AMA units is negligible, after functionalization of MMA-α-AMA copolymers by the azo coupling reaction, one can obtain azo chromophore-containing copolymers in which bulky chromophore-containing units will be separated by extended sequences of MMA units. When developing NLO materials based on these polymers, such a structure, in our opinion, should contribute to the efficiency of poling and, as a consequence, increase the NLO response.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.04.007.

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